TITLE

Ferritic Stainless Steel Having High Temperature Creep Resistance

INVENTOR

John F. Grubb

CROSS REFERENCE TO RELATED APPLICATIONS

Not applicable.

STATEMENT REGARDING FEDERALLY
SPONSORED RESEARCH OR DEVELOPMENT

Not applicable.

TECHNICAL FIELD AND INDUSTRIAL
APPLICABILITY OF THE INVENTION

The present invention is directed to a ferritic stainless steel alloy.
More particularly, the present invention is directed to a ferritic stainless steel alloy
having microstructural stability and mechanical properties making it particularly
suited for high temperature applications. Such applications include, but are not
limited to, current collecting interconnects in solid oxide fuel cells, furnace
hardware, equipment for the chemical process, petrochemical, electrical power
generation, and pollution control industries, and equipment for handling molten
copper and other molten metals.

DESCRIPTION OF THE INVENTION BACKGROUND

Fuel cells are highly efficient, environmentally friendly means for generating electric power. The basic principle behind the operation of fuel cells is the generation of electricity by the combustion of fuel. The fuel is separated

5 from an oxidizer by a permeable barrier known as an electrolyte. Hydrogen atoms on the fuel side of the electrolyte are ionized. The resulting protons pass through the electrolyte, while the liberated electrons travel through an external circuit. On the air side of the electrolyte, opposite the fuel side, two protons combine with an oxygen atom and two electrons to create a water molecule,

10 liberating heat and completing the electric circuit. Energy is extracted from the process by using the electrons in the external circuit to do work. For fuel cells which run at higher temperatures, heat liberated from the reaction on the air side can also be used for fuel reformation or heating applications, increasing the efficiency of the cell's overall operation.

15 A type of fuel cell currently attracting much interest is the solid oxide fuel cell (SOFC). SOFC's operate at high temperatures (1450-1800°F (788-982°C)), which means that they can internally reform common hydrocarbon fuels such as natural gas, diesel fuel, gasoline, alcohol, and coal gas into hydrogen and carbon monoxide. Internal reformation recycles thermal energy

20 and eliminates the need for expensive platinum group metal catalysts. Hydrogen and carbon monoxide are both used as fuel in the SOFC. Hydrogen combines with oxygen in a modification of the generic fuel cell reaction detailed previously.

The electrolyte is an oxide ceramic, which is permeable to oxygen ions (O^{2-}), rather than to protons. Thus, the SOFC runs in a reverse direction relative to certain other fuel cell types. In addition to combusting hydrogen, carbon monoxide is oxidized to carbon dioxide at the anode, releasing heat. This is an

5 advantage because carbon monoxide is present in unrefined fuels and can poison low temperature fuel cells, reduce operating efficiency. Small SOFC's operate at up to about 50% efficiency. To achieve even greater efficiency, medium sized and larger SOFC's can be combined with gas turbines. The resulting efficiency of a combined SOFC-gas turbine set can reach 70%.

10   Several variants on the basic SOFC design exist. The electrolyte is typically a form of zirconia that has been stabilized by the addition of oxides to inhibit lattice changes and provide high ionic conductivity when heated to high temperatures. Such oxide-stabilized materials are generally known, and are referred to herein, as "stabilized zirconia". SOFC's commonly include yttria-

15 stabilized zirconia (YSZ) as the stabilized zirconia electrolyte. A reported coefficient of thermal expansion (CTE) of YSZ, between 20°C (68°F) and 1000°(1832°C), is about 11 x 10^{-6} per °C.

            A tubular SOFC, of relatively simple construction, which operates at extremely high temperatures (1800°F (982°C)) and is large in size, has been

20 developed. A tubular SOFC may be scaled up in size by increasing the size and number of individual SOFC tubes in the device. More recently, the "planar" SOFC (PSOFC) has been developed. PSOFC's are relatively compact and are

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constructed of stacks of flat cells. The anode and cathode plates are typically ceramic materials. Permeable nickel-zirconia cermets have also been used for the anode.

Interconnects are needed to collect the electrons generated by a

5   fuel cell.   Interconnects also function as a physical separator for the oxidizing and reducing gas streams. Accordingly, the material used to form fuel cell interconnects should be electrically conductive, oxidation resistant, and mechanically stable, and should have thermal expansion properties substantially matching those of the ceramic components of the cell, which may be physically

10 disposed adjacent to the interconnects. Until recently, SOFC interconnects were commonly fabricated from ceramic material that is electrically conductive at high temperatures, commonly $LaCrO_3$ doped with either CaO or SrO. Although ceramics typically are stable when subjected to high temperatures for prolonged periods, ceramics also are brittle and relatively expensive, and are poor

15 conductors of electricity relative to metals. Certain metallic interconnects have been fabricated from a chromium-based alloy developed for that purpose. The alloy provides adequate oxidation resistance and a good thermal expansion match with stabilized zirconia. However, the powder metallurgical route used to produce the alloy makes it very expensive, which adds substantial cost to

20 SOFC's produced from the alloy.

Fabricating SOFC interconnects from stainless steels may provide advantages over ceramics because the steels would have greater electrical

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conductivity and may be in a form less brittle than ceramics. However, problems associated with the use of stainless steels in SOFC interconnect applications include oxidation, thermal expansion, and creep problems. Oxidation can reduce the capacity of a stainless steel to conduct current, thereby reducing cell output

5   over time. Standard austenitic stainless steels do not provide a good thermal expansion match with conventional SOFC electrolyte ceramics. Ferritic stainless steels that may provide a good thermal expansion match with the ceramic electrolytes typically exhibit low creep resistance. For example, tests conducted by the present inventor on several commercially available stainless steels,

10   including E-BRITE® (UNS S44627), AL 29-4-2® (UNS S44800) and ALFA-IV® (*Alloy Digest* SS-677, ASM International) alloys, have demonstrated that E-BRITE® alloy has acceptable thermal expansion for SOFC use, good thermal stability, and forms the desirable Cr_2O_3 oxide. The creep resistance of E-BRITE® alloy, however, is less than desirable for SOFC applications.

15   Thus, there exists a need for an improved stainless steel alloy having high temperature creep resistance, good thermal stability, and other characteristics that make it suitable for use as current collecting interconnects in SOFC's and for use in other high temperature applications, such as in equipment for the chemical process, petrochemical, electrical power generation, and

20   pollution control industries, as well as in furnace hardware and equipment for handling molten metals.

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SUMMARY OF THE INVENTION

The present invention addresses the above-described need by providing a ferritic stainless steel including greater than 25 weight percent chromium, 0.75 up to 1.5 weight percent molybdenum, up to 0.05 weight percent carbon, and at least one of niobium, titanium, and tantalum, wherein the sum of the weight percentages of niobium, titanium, and tantalum satisfies the equation $0.4 \leq (\%Nb + \%Ti + \frac{1}{2}(\%Ta)) \leq 1$. The steel of the present invention has a CTE within about 25% of the CTE of stabilized zirconia between 20°C (68°F) and 1000°C (1832°F). The steel of the present invention also exhibits at least one creep property selected from creep rupture strength of at least 1000 psi at 900°C (1652°F), time to 1% creep strain of at least 100 hours at 900°C (1652°F) under load of 1000 psi, and time to 2% creep strain of at least 200 hours at 900°C (1652°F) under load of 1000 psi.

The present invention also provides a method for making a ferritic stainless steel alloy wherein the method includes forming a steel comprising greater than 25 weight percent chromium, 0.75 up to 1.5 weight percent molybdenum, up to 0.05 weight percent carbon, and at least one of niobium, titanium, and tantalum, wherein the sum of the weight percentages of niobium, titanium, and tantalum satisfies the equation $0.4 \leq (\%Nb + \%Ti + \frac{1}{2}(\%Ta)) \leq 1$. The steel has a CTE within about 25% of the CTE of stabilized zirconia, and preferably has a CTE that is greater than and within 25% of the CTE of stabilized zirconia, between 20°C (68°F) and 1000°C (1832°F). The steel also has at least

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one creep property selected from creep rupture strength of at least 1000 psi at 900°C (1652°F), time to 1% creep strain of at least 100 hours at 900°C (1652°F) under load of 1000 psi, and time to 2% creep strain of at least 200 hours at 900°C (1652°F) under load of 1000 psi. In a subsequent step, the steel is

5   solution annealed and then cooled from the annealing temperature. Solution annealing preferably is performed at a temperature that is at least the greater of the intended service temperature of the alloy and 1600°F (871°C). If desired, the solution annealed stainless steel is precipitation heat treated to harden the steel.

The present invention also provides for the fabrication of articles of

10   manufacture from the stainless steel of the present invention. The articles may be fabricated using conventional techniques.

The stainless steel of the present invention exhibits improved high temperature mechanical properties, including improved high temperature creep resistance, relative to other ferritic stainless steels. The steel also should exhibit

15   a good thermal expansion match with YSZ, the stabilized zirconia commonly used as electrolyte in SOFC's. Thus, the steel is suitable for use in SOFC's as current carrying interconnects and flow separators and may be used in place of ceramics. The steel also may be suitable for use in high stress, high temperature applications including, for example, oxygen sensor devices, certain chemical

20   process, petrochemical, electrical power generation, and pollution control equipment, high temperature furnace hardware, and molten metal handling equipment.

The reader will appreciate the foregoing details and advantages of the present invention, as well as others, upon consideration of the following detailed description of embodiments of the invention. The reader also may comprehend additional details and advantages of the present invention upon

5   making and/or using the stainless steel of the present invention.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a graph of ASTM grain size as a function of annealing temperature for several ferritic stainless steels;

Figures 2(a)-(c) are graphs illustrating several mechanical

10   properties for several ferritic stainless steels tested at various temperatures;

Figure 3 is a graph of time to 1% creep strain as a function of applied stress for several tested ferritic stainless steels at test temperatures of (a) 800°C (1472°F), (b) 850°C (1562°F), and (c) 900°C (1652°F);

Figure 4 is a graph of time to 2% creep strain as a function of

15   applied stress for several ferritic stainless steels at test temperatures of (a) 800°C (1472°F), (b) 850°C (1562°F), and (c) 900°C (1652°F);

Figure 5 is a graph of time to rupture as a function of applied stress for several ferritic stainless steels at test temperatures of (a) 800°C (1472°F), (b) 850°C (1562°F), and (c) 900°C (1652°F);

20   Figure 6 is a graph of weight change as a function of exposure time to ambient air at (800°C (1472°F) and depicts isothermal oxidation data for several ferritic stainless steels;

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Figure 7 depicts isothermal oxidation data obtained on exposing several ferritic stainless steels to ambient air at 800°C (1472°F);

Figure 8 depicts the isothermal oxidation data obtained on exposing several ferritic stainless steels to ambient air at 900°C (1652°F); and

5   Figure 9 depicts average cycles-to-failure (CTF) values as a function of cycle temperature for 0.002" thick samples of several ferritic stainless steels.

DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION

10   It was postulated that replacing ceramic SOFC interconnects with stainless steel interconnects would offer advantages. Initial work in this area, however, revealed drawbacks in the various existing stainless steels considered. For example, austenitic nickel-base materials were found to exhibit a poor coefficient of thermal expansion ratio. Alumina-forming ferritic alloys were found

15   deficient because they are not electrically conductive after they oxidize.

The inventor also evaluated certain commercially available ferritic stainless steels offered by Allegheny Ludlum Corporation, Pittsburgh, Pennsylvania, under the trademarks AL 29-4-2®, ALFA-IV®, and E-BRITE®, at elevated temperature for their suitability as interconnects in SOFC's. AL 29-4-2®

20   alloy is described by UNS designation S44800 and is listed in several ASTM designations, including A240. The typical composition limits (in weight percentages) for AL 29-4-2® alloy are 28.0-30.0 chromium, 3.5-4.2 molybdenum,

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2.0-2.5 nickel, balance iron and residual impurities. ALFA-IV® alloy is a

proprietary alloy that is generally described in United States Patent No.

4,414,023, and has a nominal composition of 20 weight percent chromium, 5

weight percent aluminum, and 0.3 weight percent rare earth metals. E-BRITE®

5   alloy is a nominally 26 weight percent chromium, 1 weight percent molybdenum

stainless steel that is generally described in United States Patent No. 3,807,991.

AL-29-4-2® alloy was found to suffer severe embrittlement at high

temperature due to extensive precipitation of sigma phase. ALFA-IV® alloy

exhibited thermal expansion above a suitable level and was found to form an

10   undesirable non-conductive Al_2O_3 film. E-BRITE® alloy was found generally

more acceptable for SOFC interconnect applications than AL-29-4-2® and

ALFA-IV® alloys, but was still unsuitable, primarily due to unacceptably low creep

resistance at high temperatures.

A ferritic stainless steel having improved high-temperature

15   mechanical properties, including improved high-temperature creep resistance,

relative to the commercial form of E-BRITE® alloy would be advantageous in

applications such as SOFC interconnects and in other high temperature

applications. Through experimentation, the present inventor identified such a

ferritic stainless steel, including greater than 25 weight percent chromium, 0.75

20   up to 1.5 weight percent molybdenum, up to 0.05 weight percent carbon, 0.4 up

to 1 weight percent niobium. Preferably, the carbon content of the alloy is limited

to 0.005 weight percent, but, as further discussed below, the presence of niobium

or another carbide former such as titanium in the alloy should provide carbide stabilization up to the broader 0.05 weight percent limit.

The ferritic stainless steel of the present invention is further characterized in that it has at least one creep property selected from creep

5　rupture strength of at least 1000 psi at 900°C (1652°F), time to 1% creep strain of at least 100 hours at 900°C (1652°F) under load of 1000 psi, and time to 2% creep strain of at least 200 hours at 900°C (1652°F) under load of 1000 psi.

Because YSZ is a common stabilized zirconia electrolyte in SOFC's, the steel of the present invention preferably has a CTE within about

10　25% of the CTE of YSZ between 20°C (68°F) and 1000°C (1832°F). As disclosed above, the CTE of YSZ within that temperature range is about 11×10^{-6} per °C. Thus, a range within about 25% of that CTE value is about 8.25 to about 13.75×10^{-6} per °C.

Minor creep and/or stress relaxation of the metallic elements of an

15　SOFC at operating temperature will leave the device essentially stress free after some time at temperature. When the SOFC is subsequently cooled, if the CTE of the metal is less than that of the stabilized zirconia electrolyte, the metal will be placed in compression while the ceramic is placed in tension. It is well known that brittle materials preferably are loaded in compression and may fail

20　unexpectedly when loaded in tension. Thus, it is preferable that the metal have a CTE as least as great as the oxide-stabilized ceramic. Therefore, the CTE of the ferritic stainless steel of the present invention preferably is at least as great, and

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may be up to 25 percent greater than, the CTE of stabilized zirconia, such as YSZ, between 20° (68°F) and 1000°C (1832°F).   The inventor has further discovered that to optimize the properties of the ferritic stainless steel of the invention for SOFC interconnect applications, the steel preferably is

5   solution annealed and then cooled from the annealing temperature during processing. Solution annealing preferably is performed at a temperature that is at least the greater of the intended service temperature of the alloy and 1600°F (871°C). The inventor has found that annealing the alloy at excessive temperatures (for example, in excess of 2200°F (1204°C)) for extended times

10   may lead to excessive grain growth, which can impair the alloy's toughness and formability. Rapid cooling from the annealing temperature, such as is produced by water quenching, was not found to be required, but is not deleterious. Very slow cooling, such as by furnace cooling, also has not been found to be necessary. Air cooling or cooling by alternate means at an equivalent rate is

15   generally preferred. To modify certain mechanical properties of the alloy for use in applications where increased hardness is required, the solution annealed stainless steel may be precipitation heat treated by conventional means

         Chromium contributes to the oxidation resistance of the stainless steel and to its formation of a Cr_2O_3 scale that is electrically conductive at high

20   temperatures. It also is largely responsible for reducing thermal expansion of the steel so that it generally matches that of zirconia. It is believed that steels including less than about 25 weight percent chromium would not exhibit these

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desired properties. As chromium content is increased above about 35 weight percent, however, the steel becomes more difficult to hot work and, therefore, more expensive to produce. Moreover, a steel including such a high chromium content would be more likely to from an undesirable intermetallic sigma (FeCr)

5   phase. Accordingly, the chromium content preferably is no greater than about 35 weight percent, more preferably is no greater than about 30 weight percent, and even more preferably is no greater than about 27.5 weight percent.

Molybdenum reduces thermal expansion. It also provides solid solution strengthening and in conjunction with niobium forms the strengthening

10   Laves phase $Fe_2(Nb,Mo)$ precipitate. Molybdenum, however, substantially increases the tendency of the stainless steel to precipitate the undesirable sigma phase, as well as the equally undesirable chi (Fe,Cr,Mo) phase. Molybdenum also impairs the oxidation resistance of the steel and can, under certain circumstances, promote a catastrophic form of oxidation. For these reasons, the

15   molybdenum content of the stainless steel preferably is carefully controlled. A molybdenum content of about 0.75 up to about 1.5 weight percent, and more preferably up to about 1.2 weight percent, provides a particularly suitable balance between the desirable and undesirable influences of the element on the alloy's properties. In particular, experimental alloys produced by the inventor including

20   0.9 to 1.1 weight percent molybdenum exhibited a particularly desirable balance of properties.

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The role of carbon in ferritic stainless steels is well known. Carbon contents less than about 0.010 weight percent are required to obtain ductility in unstabilized alloys. To optimize properties, carbon contents less than 0.005 weight percent are needed. The niobium content of the stainless steel of the

5   present invention, however, will mitigate many of the effects of the carbon. For this reason, carbon contents up to about 0.05 weight percent are acceptable if sufficient carbide forming elements are present to stabilize the carbon content. One having ordinary skill in the art may readily determine the content of carbide forming elements that must be present in a given alloy of the present invention to

10   stabilize a given carbon content. If welded articles are to be formed from a steel of the present invention, it may be preferable to respect the preferred 0.005 weight percent upper limit to prevent hot cracking of the welds.

Small additions of niobium have been found to improve creep or "sag" resistance in ferritic stainless steels. These niobium additions, under the

15   right circumstances, produce a fine dispersion of Laves phase ($Fe_2(Ta,Nb,Mo)$) precipitates. The suitable content of niobium in the stainless steel of the invention was determined through experimentation, as described below. It is believed that titanium may be substituted for a portion of the niobium in the alloy. In addition, tantalum is similar to niobium in its influence on the properties of the

20   alloy, but is heavier and substantially more costly than niobium. It is believed that tantalum may be substituted for niobium and titanium in whole or in part on the basis that 2 weight percent tantalum is equivalent to 1 weight percent

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niobium and titanium. Thus, it is believed that the improved properties of the stainless steel of the invention observed by the inventor may be achieved by including in the steel at least one of niobium, titanium, and tantalum, wherein the sum of the weight percentages of niobium, titanium, and tantalum satisfies the

5   following equation:

$$0.4 \leq (\%Nb + \%Ti + \tfrac{1}{2}(\%Ta)) \leq 1$$

Preferably, the steel of the invention includes no more than 0.50 weight percent titanium.

One benefit of adding titanium to the stainless steel of the present

10   invention is that it will remove nitrogen from solution as TiN. This will better prevent the formation of NbN and CrNbN precipitates, thus preserving the niobium (a more costly alloying addition than titanium) for the formation of desirable Laves (Fe_2Nb) phase strengthening precipitates. It is also believed that the addition of titanium may similarly remove carbon from solution and thereby

15   better prevent formation of NbC and NbCN. It also has been observed that titanium in amounts above about 0.07 weight percent appears to mitigate the problem of niobium-induced weld cracking.

To better ensure a significant improvement in high temperature properties while limiting costs associated with the alloying additions, the sum of

20   the weight percentages of niobium, titanium, and tantalum in the steel of the present invention is more narrowly controlled to satisfy the following equation:

$$0.5 \leq (\%Nb + \%Ti + \tfrac{1}{2}(\%Ta)) \leq 0.75$$

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wherein the maximum and preferred contents of titanium are the same as for the previous equation.

In addition, to the foregoing elements, the ferritic stainless steel of the present invention may include additions of one or more rare earth elements. These optional rare earth additions include, but are not limited to, up to about 0.1 weight percent cerium and up to 0.05 weight percent lanthanum. Additions of rare earth elements as alloy additions have been shown to be highly beneficial for increasing the oxidation resistance of iron-base alloys. Such effect has been demonstrated for yttrium, lanthanum, and cerium. The other rare earth elements tend progressively to be more costly and less effective, but can be used for that purpose. It is not necessary to add only a single rare earth metal (REM) when adding such elements to the stainless steel of the present invention. The commercially produced mixture of REM elements known as mischmetal can be used to provide economical REM doping. As is known in the art, mischmetal is a naturally derived mixture of metallic rare earth elements containing about 50 weight percent cerium, with the remainder principally lanthanum and neodymium.

Various mechanisms have been proposed for the effect of rare earth elements on the oxidation resistance of metal alloys. Currently, the most widely accepted mechanism is based on the modification of internal surfaces, such as oxide/oxide grain boundaries and oxide/metal interface. A modification to this mechanism is the "poisoned interface" model, in which REM atoms tie up sulfur at the oxide/metal interface. Acceptance of this mechanism is supported

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by the finding that reducing sulfur in REM-free alloys to ultra-low levels (less than 1 ppm) has much the same effect as adding REM to alloys with typical sulfur contents (3-100 ppm). Other theories that have been proposed include increased scale plasticity, promotion of protective oxide formation, and

5   mechanical keying of the scale to the metal by formation of rare earth oxide pegs. Regardless of the actual mechanism, it is the increased corrosion resistance offered by REM addition that is significant to the present invention. It is important not to add too great an amount of REM, because these elements have limited solubility in iron-based alloys, and the excess solute forms

10   undesirable intermetallic phase, deep eutectics, or both, with very significant impairment of hot workability. High levels of REM also may lead to "overdoping", which is characterized by the formation of islands of REM oxides and increased oxidation rates.

The addition of other non-REM elements also may provide

15   enhanced oxidation resistance. In particular, hafnium provides a benefit similar to that provided by REM addition. Hafnium is, however, very expensive. Zirconium is of much lower cost and can be substituted in amounts similar to hafnium, although zirconium is less effective. Just as with the REM elements, the amount of zirconium and/or hafnium included in the alloy should not be too

20   great or excessive amounts of undesirable intermetallic phases will be formed. Therefore, hafnium and/or zirconium may be included in the alloy in a combined amount that is up to about 0.05 weight percent.

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Additions of other alloying elements and additives as are known in the art to improve or provide additional characteristics to the alloy also may be made. Such additions include, for example, silicon, aluminum, tungsten, and manganese. Silicon is used in steelmaking as a deoxidizer. It promotes the

5   precipitation of Laves phase, but also the undesirable sigma phase. In solid solution, silicon hardens ferrite and makes it brittle. Thus, if present, the silicon content of the present alloy preferably is limited to less than about 1 weight percent, and more preferably is less than about 0.5 weight percent.

Aluminum is both a deoxidizer and a hardener. Since aluminum is

10   a more effective deoxidizer than silicon, a lower residual content of aluminum is required to produce complete oxidation. Aluminum content, if present, preferably is less than about 0.25 weight percent, and more preferably will be in the range of about 0.002 to about 0.05 weight percent.

Tungsten is generally similar to molybdenum in effect, but is

15   heavier, more expensive, and more difficult to melt into the alloy. It may be introduced along with molybdenum, but if present is preferably held to levels less than about 0.25 weight percent.

Manganese is intentionally added to carbon steels for the mitigation of sulfur-induced hot shortness. It is typically present in stainless steels, but in

20   the present alloy preferably is limited to less than about 1 weight percent, and more preferably is limited to less than about 0.5 weight percent.

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Unavoidable impurities may be present in the stainless steel of the invention. Among those of significance are nitrogen, copper, sulfur, and phosphorus. Molten Fe-Cr alloys readily absorb nitrogen when in contact with air. As such an alloy's chromium content is increased above about 18 weight

5   percent, removal of nitrogen becomes increasingly difficult. Nitrogen in ferritic stainless steels frequently produces embrittlement, either through chromium or aluminum nitride precipitation. The nitrogen content of the steel of the present invention preferably is limited to less than about 0.04 weight percent, and is more preferably limited to less than about 0.010 weight percent. Sulfur is an inevitable

10   impurity in steelmaking, and one that is generally undesirable. It is easily removed during argon oxygen decarburization (AOD) refining, but not during vacuum induction melting (VIM) refining. As is known to those of ordinary skill in the art, AOD is a secondary refining process for the controlled oxidation of carbon in a steel melt in which oxygen, argon, and nitrogen are injected into a

15   molten metal bath through submerged, side-mounted tuyeres. VIM is a refining and remelting process in which metal is melted inside a vacuum chamber by induction heating.

Sulfur is preferably reduced to the lowest readily attainable level, and in any case preferably should be no more than about 0.010 weight percent.

20   Phosphorus is a solid solution strengthener of steels, and may produce brittleness. Phosphorus is not readily removed from stainless steels, so cannot easily be reduced to extremely low levels, but preferably is restricted to less than

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about 0.050 weight percent. Copper is not readily removed during steelmaking,

but is mostly innocuous. High levels of copper (greater than about 2 weight

percent) impair the hot ductility and hot workability of ferritic stainless steels. In

E-BRITE® alloy, copper is limited to no more than about 0.025 weight percent to

5   better provide resistance to stress corrosion cracking (SCC) in boiling

magnesium chloride solutions. High resistance to SCC is not a specific goal of

the present invention, and copper is preferably limited to less than about 0.25

weight percent.

Prior to performing tests to determine the properties of various

10   ferritic stainless steels, six fifty-pound heats, designated WC70 through WC75,

having the compositions set forth in Table 1 below, were prepared by VIM. All

figures shown are weight percentages of the entire heat weight.

TABLE 1

Heat	WC70	WC71	WC72	WC73	WC74	WC75
C	0.0026	0.0026	0.0038	0.0022	0.0023	0.0033
Mn	0.054	0.055	0.060	0.049	0.052	0.053
P	0.010	0.010	0.010	0.010	0.010	0.010
S	0.0029	0.0027	0.0014	0.0011	0.0003	0.0006
Si	0.16	0.15	0.14	0.15	0.15	0.15
Cr	25.52	25.98	25.63	25.77	25.69	25.79
Ni	0.096	0.094	0.095	0.094	0.094	0.095
Mo	1.05	1.05	1.03	1.04	1.04	1.04
Al	0.002	0.002	0.002	0.002	0.002	0.002
Nb	0.12	0.68	0.13	0.68	0.71	0.71
Ce	<0.001	<0.001	0.001	0.003	0.042	0.009
La	<0.001	<0.001	0.001	0.001	0.016	0.003
Zr	<0.001	<0.001	<0.001	<0.001	<0.001	0.011
N	0.0010	0.0010	0.0008	0.0009	0.0011	0.0011

Heats WC70 and WC72 are representative of a standard ferritic stainless steels having 0.37 weight percent or less niobium and 0.001 weight percent or less of each of cerium, lanthanum, and zirconium. The compositions found in the heats WC70 and WC72 are typical of E-BRITE® ferritic stainless steel. Heats WC71, WC73, WC74, and WC75 have the general composition of the standard alloy, with the following modifications made by the present inventor: the WC71 heat includes increased niobium content; the WC73 heat includes niobium and cerium; the WC74 heat includes niobium, cerium, and lanthanum; and the WC75 heat includes niobium, cerium, lanthanum, and zirconium. In Table 1, the use of "<0.001" in connection with cerium, lanthanum, and zirconium indicates that no intentional addition of these elements was made and that

chemical analysis showed that the alloys lacked any significant amount of the elements. As discussed below, the present inventor's modifications to the standard E-BRITE® alloy composition provide significant improvement in microstructural stability, mechanical properties, and high temperature creep

5   resistance.

The heats of Table 1 were cast to ingots and processed prior to testing. Each ingot was cross rolled at 2200°F (1204°C), spreading the ingot to a bar 5 inches (127 mm) in width. As is known in the art, cross rolling is the rolling of metal article in rolling directions of about ninety degrees from the direction of a

10   previous rolling. The cross rolled bar was then hot rolled at a temperature of at least 2100°F (1149°C) with a sufficient number of passes through a series of rolling stands to provide a 0.125 inch (3.18 mm) thick band. The hot rolled band was then water quenched, shot blasted, pickled clean, and then cold rolled to a 0.040 inch (1.02 mm) thick strip.

15   Following cold rolling, samples of the strip formed from each of the Table 1 heats were retained for recrystallization studies. The remainder of each strip was line annealed at 1980°F (1082°C) (WC71-WC75 alloys) or at 1725°F (941°C) (WC70 alloy) for 30 seconds time-at-temperature. Following annealing, each strip was descaled by brief immersion in molten sodium salts, and then

20   pickled clean in a mixture of sulfuric, nitric, and hydrofluoric acids. A portion of the annealed 0.040 (1.02 mm) thick material was further cold rolled to foil (0.002 inch/0.051 mm thick) for strip life cyclic oxidation testing.

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A variety of tests, discussed below, were performed on the fully processed strips formed from each heat to determine the microstructural stability, mechanical properties, creep/rupture strength, and oxidation resistance of the six alloy compositions at temperatures representative of SOFC operation.

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I.   Recrystallization Study

Samples of the 0.040 (1.02 mm) thick strip from each heat, which had previously been annealed, pickled and cold rolled, were evaluated for microstructural stability. Coupons from each heat were annealed in a muffle

10   furnace at temperatures ranging from 1750-2000°F (954-1093°C) for thirty seconds time-at-temperature to simulate production continuous anneal exposures. Longitudinal sections were then mounted and polished for metallographic examination. Grain size was evaluated per ASTM standard E112 both at the sample centerline and near the sample surface. Tables 2 (centerline

15   measurements) and 3 (measurement near sample surface) provide ASTM grain size results. Grain size measurements differing at two different points on the same sample are indicated as, for example, "7.0/7.5". The larger the grain size number, the smaller the grain size.

TABLE 2 – Centerline Measurements

Annealing Temperature	Heat Number					
	WC70	WC71	WC72	WC73	WC74	WC75
1750°F (954°C)	7.0 / 7.5	–	7.0 / 7.5	–	–	–
1800°F (982°C)	7.5	–	7.0 / 7.5	–	–	–
1850°F (1010°C)	7.0 / 8.0	–	5.0 / 6.5	–	–	–
1900°F (1038°C)	6.0 / 7.5	–	4.5	–	–	–
1950°F (1066°C)	4.5 / 7.0	–	4.0 / 4.5	–	–	–
2000°F (1093°C)	3.0 / 5.5	6.5 / 7.5	4.0	6.0 / 6.5	–	6.5 / 7.0
2050°F (1121°C)	3.0 / 4.0	3.0 / 5.0	2.5	4.0	4.0 / 5.0	5.0 / 6.0
2100°F (1148°C)	2.0 / 2.5	3.0	2.5	3.5	3.5 / 4.0	2.0 / 3.5

As indicated by the results of Table 2, which include measurements taken at the sample centerline after annealing, the alloy of heats WC70 and

5   WC72, which have only trace levels of niobium and rare earth elements, readily recrystallized at 1750°F (954°C) and experienced significant grain growth at temperatures of about 1950°F (1066°C) and above. The alloys having greater than trace amounts of niobium (heat WC71), niobium and cerium (heat WC73), and niobium, cerium, lanthanum, and zirconium (heat WC75) did not show

10   evidence of recrystallization until about 2000°F (1093°C). The alloy containing greater than trace amounts of niobium, cerium, and lanthanum (heat WC74) did not show recrystallization until about 2050°F (1121°C). These results show that the addition of niobium, either alone or in conjunction with rare earth elements and zirconium, delays recrystallization by a minimum of 200°F (93°C) as

15   compared to the unmodified form of the ferritic alloy.

TABLE 3 – Measurements at Sample Surface

Annealing Temperature	Heat Number					
	WC70	WC71	WC72	WC73	WC74	WC75
1750°F (954°C)	8.5 / 9.5	–	9.0	–	–	–
1800°F (982°C)	8.5 / 9.0	–	8.5	–	–	–
1850°F (1010°C)	6.0 / 7.5	–	8.0	–	–	–
1900°F (1038°C)	7.0 / 7.5	–	7.5	–	–	–
1950°F (1066°C)	4.5 / 7.0	–	4.0 / 4.5	–	–	–
2000°F (1093°C)	5.0 / 5.5	8.0	4.0	7.5	–	7.5 / 8.0
2050°F (1121°C)	3.0 / 4.0	7.5	2.5	6.5	4.0 / 5.0	7.0
2100°F (1148°C)	2.0 / 2.5	3.0	2.5	7.0	3.5 / 4.0	2.0 / 3.5

The results shown in Table 3, which includes grain size

measurements taken near the sample surface after annealing, are quite similar to

those in Table 2. It should be noted that the sample of heat WC71 tested at

1750°F (954°C) represents a non-equiaxed microstructure. The samples having

a standard ferritic stainless steel composition, heats WC70 and WC72, did

exhibit recrystallization beginning at about 1750°F (954°C), and significant

recrystallization was observed at 1950°F (1066°C) and above. Again, the

inventor's modified ferritic alloys did not show recrystallization until above 1950°F

(1066°C), with the niobium, cerium, and lanthanum-containing alloy (heat WC74)

exhibiting no evidence of recrystallization until 2000°F (1093°C). Accordingly,

the addition of niobium, either alone or in conjunction with zirconium and rare

earth elements including, but not limited to, cerium and lanthanum, delayed

recrystallization by at least 200°F (93°C).

Figure 1 graphically demonstrates the effect of the addition of niobium, alone or in combination with rare earth elements, on the recrystallization of the various alloys. As indicated above in the discussion of Tables 2 and 3, recrystallization is delayed by at least 200°F (93°C) in the alloys having

5   increased niobium, either alone or in addition to one or more rare earth elements, including cerium, lanthanum, and zirconium.

Without intending to be bound to any particular theory, it appears that the modified alloys' (including WC73-WC75) resistance to recrystallization is the result of the presence of Laves phase precipitates in the samples. Laves

10   phase is an intermetallic phase that contributes to abrasion resistance, but that severely limits an alloy's material ductility and impact resistance. Metallographic analysis of annealed 0.040 inch (1.02 mm) thick material revealed that the standard alloy (heat WC70) contains few Laves phase precipitates, while the modified alloys tested contained a significant fraction of Laves phase distributed

15   within grains and on grain boundaries. These precipitates interfere with grain boundary motion and so impede grain growth. Thus, the modified alloys have greater grain size stability than does the standard alloy.

II.   Mechanical Testing

20   Tensile specimens were machined from 0.040 inch (1.02 mm) thick annealed strip and tested. Elevated temperature testing was done in ASTM E21.

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Longitudinal tensile properties, calculated as the average properties of a minimum of two samples per alloy, are shown in Table 4 and Figure 2.

TABLE 4

Heat	Test temperature	Hardness (R$_b$)	Yield stress (psi)	Tensile stress (ksi)	Elongation (%)
	77°F (25°C)	79.0	49,600	76,500	27
WC70	1472°F (800°C)		4,367	6,767	67
	1562°F (850°C)		4,533	5,600	98
	1652°F (900°C)		3,100	4,233	76
	77°F (25°C)	84.0	52,900	80,000	27
WC71	1472°F (800°C)		7,300	10,160	50
	1562°F (850°C)		4,433	6,700	30
	1652°F (900°C)		3,475	5,450	56
	77°F (25°C)	84.4	51,300	79,700	26
WC73	1472°F (800°C)		5,800	8,520	46
	1562°F (850°C)		5,600	7,567	50
	1652°F (900°C)		3,567	5,733	58
	77°F (25°C)	84.6	49,300	80,900	23
WC75	1472°F (800°C)		6,567	9,733	56
	1562°F (850°C)		4,950	7,275	67
	1652°F (900°C)		3,433	5,667	85

As shown in Table 4 and Figure 2, the modified heats (heats WC71, WC73, and WC75) exhibited higher yield and ultimate tensile strength values at elevated temperatures, at the expense of generally slightly reduced elongation (0.2% offset). Samples that broke on or outside gauge marks were excluded from the average elongation calculation.

As seen in Table 4, yield strength was greater for the modified alloys (heats WC71, WC73, and WC75) than for the standard alloy (heat WC70)

27

at each test temperature, with one exception. The only anomalous result was seen with the heat WC71 alloy at 1562°F (850°C).

Tensile strength was greater for the modified alloys than for the standard alloy at all elevated temperatures without exception. Typically, alloy
5   hardness is analogous to alloy tensile strength. Such was the case in the present situation. In looking at Table 4, one observes that the modified alloys not only have a greater hardness value than the standard alloy, but also have a greater tensile strength. Accordingly, the modified alloys possess mechanical properties superior to those of the standard alloy.

10   III.   <u>Creep and Stress Rupture Testing</u>

Creep is time-dependent strain occurring under stress. Creep strain occurring at a diminishing rate is called primary creep; that occurring at a minimum and almost constant rate, secondary creep; and that occurring at an accelerating rate, tertiary creep. Creep of SOFC interconnects at elevated
15   temperatures can cause a loss of cell integrity, resulting in gas leakage. Creep strength is the stress that will cause a given creep strain in a creep test at a given time in a specified constant environment. The creep strength of the standard E-BRITE® alloy, such as is embodied in heats WC70 and WC72, has been determined to be inadequate in the temperatures and stresses encountered in
20   SOFC applications. The inventive modifications made to the standard alloy, however, have been shown to significantly improve creep resistance.

Creep-rupture strength is the stress that causes fracture in a creep test at a given time, in a specified constant environment. A test for creep-rupture is one in which progressive specimen deformation and the time for rupture are both measured. Creep-rupture testing was performed using 0.040 inch (1.02

5   mm) thick material from the standard alloy (heat WC70) and from modified alloys (heats WC71, WC73, and WC75). The standard alloy samples were annealed at 1715-1735°F (935-946°C) for 60 seconds time-at-temperature to yield an ASTM grain size of 8-9. Samples of the three modified alloys were annealed at 1970-1990°F (1077-1088°C) for 30 seconds time-at-temperature and had grain sizes

10   of approximately ASTM 8. The goal of the test was to evaluate the effect on creep strength of the alloying additions in the modified alloys. Because grain size has been shown to be of great importance with respect to creep and creep-rupture resistance, the fact that both the modified and unmodified alloys had similar grain size (within 1-2 ASTM grain size numbers) demonstrates that the

15   observed variations in creep resistance are due to composition and precipitation state.

Creep-rupture blanks were machined from 0.040 inch (1.02 mm) thick annealed strip in the longitudinal direction. Creep-rupture tests were conducted according to ASTM E139 to determine the time to 1% creep strain

20   (Figures 3(a)-(c)), 2% creep strain (Figures 4(a)-(c)), and rupture (Figures 5(a)-(c)) at 800°C (1472°F), 850°C (1562°F), and 900°C (1652°F) for times up to 1000 hours and at applied stresses up to 3500 psi. Results are presented in

Figures 3-5. The data included in Figures 3-5 is provided in the following Tables 5-16.

TEMPERATURE	STRESS (psi)	TIME(hrs)
	2,000	125.0
	2,500	120.0
	2,800	3.8
1472°F (800°C)	3,000	50.0
	3,100	11.0
	3,200	6.8
	3,500	4.8
	1,500	110.0
	1,800	4.0
1562°F(850°C)	2,000	23.0
	2,200	8.0
	2,500	6.0
	700	300.0
	750	3.8
	750	5.0
	800	4.0
	800	4.0
1652°F(900°C)	900	2.5
	1,100	1.0
	1,100	1.0
	1,300	2.3
	1,500	1.0
Table 5 Heat WC70, time to 1% creep strain		

30

TEMPERATURE	STRESS (psi)	TIME(hrs)
	2,000	1000.0
	2,500	320.0
	2,800	9.5
1472°F (800°C)	3,000	160.0
	3,100	31.0
	3,200	15.5
	3,500	9.8
	1,500	300.0
	1,800	8.8
1562°F(850°C)	2,000	39.5
	2,200	17.5
	2,500	23.0
	700	400.0
	750	15.0
	750	15.0
	800	8.0
	800	8.0
1652°F(900°C)	900	5.0
	1,100	2.0
	1,100	2.0
	1,300	4.5
	1,500	1.5

Table 6 Heat WC70, time to 2% creep strain

TEMPERATURE	STRESS (psi)	TIME(hrs)
	2,500	822.5
	2,800	77.5
	3,000	537.4
1472°F (800°C)	3,100	160.1
	3,200	72.5
	3,500	58.2
	1,400	229.5
	1,500	520.3
	1,750	143.7
1562°F(850°C)	1,800	145.9
	2,200	48.3
	2,500	106.5
	700	2205.0
	750	326.5
	800	177.4
1652°F(900°C)	900	156.1
	1,100	61.2
	1,300	25.1
	1,500	37.8

Table 7 Heat WC70, time to rupture

5

TEMPERATURE	STRESS (psi)	TIME(h)
	2,000	370.0
	2,200	350.0
	2,300	87.5
1472°F (800°C)	2,450	185.0
	2,500	14.0
	3,000	30.0
	1,700	92.5
	1,800	75.0
1562°F(850°C)	2,000	53.0
	2,500	11.3
	1,500	66.0
	1,600	28.0
1652°F(900°C)	1,700	22.0
	1,800	7.5
	2,000	5.0

Table 8 Heat WC71, time to 1% creep strain

TEMPERATURE	STRESS (psi)	TIME(hrs)
	2,000	650.0
	2,200	505.0
	2,300	156.3
1472°F (800°C)	2,450	285.0
	2,500	29.0
	3,000	48.0
	1,700	192.5
	1,800	180.0
1562°F(850°C)	2,000	101.0
	2,500	21.0
	1,500	86.0
	1,600	60.0
1652°F(900°C)	1,700	33.0
	1,800	12.5
	2,000	10.0

Table 9 Heat WC71, time to 2% creep strain

5

TEMPERATURE	STRESS (psi)	TIME(hrs)
	2,200	954.4
	2,300	379.8
1472°F (800°C)	2,450	662.4
	2,500	239.8
	3,000	131.0
	1,700	372.0
	1,800	652.9
1562°F(850°C)	2,000	287.0
	2,500	45.5
	1,500	203.4
	1,600	175.0
	1,600	188.9
1652°F(900°C)	1,700	83.0
	1,800	37.8
	2,000	56.2

Table 10 Heat WC71, time to rupture

TEMPERATURE	STRESS (psi)	TIME(hrs)
	2,500	210.0
	2,600	200.0
1472°F (800°C)	2,800	120.0
	3,000	75.0
	3,200	375.0
	3,350	60.0
	1,500	390.0
	1,750	500.0
	1,850	410.0
1562°F(850°C)	1,900	122.0
	2,000	36.0
	2,500	2.3
	1,000	435.0
	1,150	75.0
	1,200	35.0
1652°F(900°C)	1,400	62.5
	1,600	57.0
	1,800	6.8
	2,000	2.3

Table 11 Heat WC73, time to 1% creep strain

TEMPERATURE	STRESS (psi)	TIME(hrs)
	2,500	355.0
	2,600	365.0
1472°F (800°C)	2,800	161.3
	3,000	127.5
	3,200	380.0
	3,350	90.0
	1,500	870.0
	1,750	745.0
	1,850	503.8
1562°F(850°C)	1,900	185.0
	2,000	77.0
	2,500	5.1
	1,000	742.5
	1,150	137.5
	1,200	88.0
1652°F(900°C)	1,400	125.0
	1,600	71.0
	1,800	13.5
	2,000	5.0

Table 12 Heat WC73, time to 2% creep strain

5

TEMPERATURE	STRESS (psi)	TIME(hrs)
	2,500	862.4
	2,600	807.2
1472°F (800°C)	2,800	310.3
	3,000	292.4
	3,200	390.2
	3,350	200.0
	1,750	894.3
	1,850	557.5
1562°F(850°C)	1,900	226.5
	2,000	266.1
	2,500	39.3
	1,150	316.6
	1,200	270.0
1652°F(900°C)	1,400	270.5
	1,600	132.0
	1,800	52.5
	2,000	24.5

Table 13 Heat WC73, time to rupture

5

TEMPERATURE	STRESS (psi)	TIME(hrs)
	2,350	225.0
	2,500	825.0
1472°F (800°C)	2,550	130.0
	2,650	50.0
	2,750	145.0
	2,800	62.5
	3,000	47.0
	1,400	8.0
	1,500	400.0
	2,000	360.0
1562°F(850°C)	2,050	102.0
	2,150	32.0
	2,200	60.0
	2,500	19.0
	1,000	1125.0
	1,100	105.0
	1,200	6.5
1652°F(900°C)	1,400	40.0
	1,500	27.0
	1,800	4.5
	2,000	3.5

Table 14 Heat WC75, time to 1% creep strain

TEMPERATURE	STRESS (psi)	TIME(hrs)
	2,350	365.0
	2,550	240.0
1472°F (800°C)	2,650	102.5
	2,750	188.0
	2,800	118.8
	3,000	72.5
	1,400	17.0
	1,500	665.0
	2,000	550.0
1562°F(850°C)	2,050	140.0
	2,150	56.0
	2,200	74.0
	2,500	48.0
	1,000	315.0
	1,100	152.5
	1,200	15.0
1652°F(900°C)	1,400	78.0
	1,500	42.5
	1,800	10.0
	2,000	6.5

Table 15 Heat WC75, time to 2% creep strain

5

TEMPERATURE	STRESS (psi)	TIME(hrs)
	2,350	858.5
	2,550	494.4
1472°F (800°C)	2,650	245.7
	2,750	253.9
	2,800	293.5
	3,000	147.0
	2,050	269.8
	2,100	140.0
	2,200	171.4
1562°F(850°C)	2,500	75.6
	1,100	470.0
	1,200	64.2
1652°F(900°C)	1,400	180.3
	1,500	131.1
	1,800	58.4
	2,000	40.4

Table 16 Heat WC75, time to rupture

Considering Figures 3-5, compositional modifications do not appear
to make a substantial difference in creep resistance at the lowest test
temperature, 800°C (1472°F). Increasing the temperature to 850°C (1562°F)

5   resulted in some differentiation between the creep resistance of standard and
modified alloys. Testing at 900°C (1652°F) revealed a clear separation of creep
strength performance between the various alloys. The modified alloys (heats
WC71, WC73, and WC75) demonstrated generally increased resistance to creep
at higher test temperatures in comparison to the standard alloy (heat WC70).

10   Results were consistent at high test temperatures for tests performed to
determine time to 1% creep, 2% creep, and rupture, with the modified alloys
demonstrating superior creep resistance compared to the standard alloy. For
example, based on the test data it will be seen that the modified alloys exhibited
a creep rupture strength of at least 1000 psi at 900°C (1652°C) for 400 hours, a

15   time to 1% creep strain of at least 100 hours at 900°C (1652°C) under load of
1000 psi, and a time to 2% creep strain of at least 200 hours at 900°C (1652°F)
under load of 1000 psi. In contrast, based on the test data the standard alloy
(WC70) exhibited creep rupture life of only about 156 hours at the lower stress of
900 psi at 900°C (1652°F). The standard alloy of heat WC70 also exhibited 1%

20   creep strain in 2.5 hours at 900°C (1652°F) under load of 900 psi, and a time to
2% creep strain of only 5.0 hours at 900°C (1652°F) under load of 900 psi.

These differences illustrate the substantial improvements in creep and rupture

resistance that result from the alloy modification.

The modified alloys' improved resistance to creep in high

temperature environments makes the alloys suitable for use in SOFC's, as well

5   as other high temperature applications.

IV.   Oxidation Testing

The isothermal oxidation behavior of the various alloys (heats

WC70-WC75) was investigated. Duplicate alloy samples were exposed for 500

hours at 800°C (1472°F) and 900°C (1652°F). The samples were first degreased

10   to remove grease and oils from the surface of the metal. Next, the samples were

weighed, placed in alumina crucibles, and exposed for set lengths of time to high

temperatures in ambient laboratory air in a box furnace constructed with a solid

hearth. Periodically, the samples were removed, weighed, and returned to the

test furnace. The measured weight changes were divided by the area of the

15   sample, resulting in a curve of specific weight change (mg/cm^2) as a function of

time.

As shown in Figure 6, isothermal oxidation testing at 800°C

(1472°F) resulted in similar weight changes for all of the samples. The standard

alloy heat (heat WC70) exhibited a slightly higher weight gain after 336 hours.

20   However, after 500 hours the weight gain was similar among all samples. As

there was no evidence of scale spallation (separation of particles from the

surface in the form of flakes), the skewed data point in Figure 5 of the heat WC70

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sample at 336 hours may have been caused by an inaccurate measurement. All of the specimens exhibited a uniform charcoal gray color with no evidence of discoloration or localized attack.

As shown in Figure 7, isothermal oxidation testing at 850°C

5   (1562°F) was limited to three samples, heats WC70, WC71, and WC74. The sample from heat WC71, which was modified relative to the standard alloy solely in niobium content, exhibited a higher weight gain than either the standard alloy (heat WC70) or the alloy modified with additions of niobium, cerium, and lanthanum (heat WC74). This difference was discernable after 168 hours and

10   became more evident after 500 hours.

As depicted by Figure 8, exposures at 900°C (1652°F) displayed results similar to those seen at the lower temperatures. Once again, the alloy modified solely by addition of niobium (heat WC71) exhibited a slightly higher weight gain than either the standard alloy (heat WC70) or the modified alloy

15   containing increased niobium, cerium, and lanthanum (heat WC74). The specimens formed a relatively uniform charcoal gray oxide scale with a greenish undertone. Some evidence of localized discoloration was perceptible.

The parabolic rate constant is a measure of the rate of oxidation. The constant summarizes an entire weight change curve at a given temperature.

20   The parabolic rate equation is of the form: $\Delta M/A = k_p \sqrt{t}$, where $\Delta M/A$ = specific weight change in mg/cm^2, t = time, and k_p = parabolic rate constant. Parabolic

rate constants from 500 hour oxidation exposure trials on each of the alloys are

listed below in Table 17.

TABLE 17

Exposure Temperature	Rate constant (g^2/ cm^{4}h)					
	WC70	WC71	WC72	WC73	WC74	WC75
1472°F / 800°C	-13.5	-13.7	-13.8	-13.9	-13.8	-13.7
1652°F / 900°C	-12.1	-11.9	-12.5	-12.2	-12.2	-12.2

5   The calculated values are essentially within the scatter ($\pm$0.25 on a logarithmic

scale) for the exposures performed.

Oxidation under conditions of thermal cycling is generally more

severe than oxidation at a constant temperature. A significant difference usually

10   exists in the coefficient of thermal expansion of oxides and metals. This can lead

to the generation of high levels of stress during thermal cycling, resulting in the

premature detachment of the protective oxide layer, known as spallation. Oxide

spallation exposes bare metal, which then rapidly re-oxidizes. Samples of the

modified alloy heats were rolled to 0.002 inch (0.051 mm) thick foil and stamped

15   into cyclic oxidation test specimens. These samples were then tested. An

electrical current was used to heat the samples for two minutes, and the samples

were then rapidly cooled to room temperature. After two minutes at ambient, the

samples were cycled back to a test temperature. The total number of cycles

before filament breakage, caused by through-thickness oxidation, is used as a

20   measure of resistance to oxidation under cyclic conditions. Samples were tested

in duplicate at 2100°F (1149°C), 2200°F (1204°C), and 2300°F (1260°C). The

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results depicted in Figure 9 indicate that the heat modified with addition of niobium (heat WC71) exhibited poor cyclic oxidation resistance, continuing the general trend noted in the isothermal oxidation tests. (CTF in Figure 9 is "cycles to failure.")

5   V.   <u>Coefficient of Thermal Expansion</u>

As discussed above, CTE is a critical property of fuel cell interconnect materials. If the mismatch between the CTE's of the interconnect and the ceramic components of the fuel cell is too great, the mechanical integrity of the cell, particularly the seals between cell layers, can be compromised.

10   Accordingly, in the stainless steel of the present invention, the CTE is within a range of about 25% of the CTE of stabilized zirconia, the conventional electrolyte in SOFC's, between 20° (68°F) and 1000°C (1832°F). For reasons described above, it is preferred that the CTE of the steel is at least as great, and may be up to about 25% greater than, the CTE of stabilized zirconia between 20°C (68°F)

15   and 1000°C (1832°F).

Samples of conventional E-BRITE® alloy were tested to determine average CTE. E-BRITE® alloy (UNS S44627) includes, in weight percent, 0.010 max. carbon, 0.40 max. manganese, 0.020 max. phosphorus, 0.020 max. sulfur, 0.40 max. silicon, 25.0-27.5 chromium, 0.50 max. nickel, 0.75-1.50 molybdenum,

20   0.015 max. nitrogen, 0.20 max. copper, 0.05-0.20 niobium, and 0.50 max. (nickel + copper). The CTE test results are provided in Table 18 below.

TABLE 18

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		Testing Laboratory A (x 10^{-6}/°C)		Testing Laboratory B (x 10^{-6}/°C)	
Test Temperature		Longitudinal	Transverse	Longitudinal	Transverse
(°C)	(°F)				
40	104	--	--	8.21	10.22
100	212	9.93	9.28	9.37	10.04
200	392	10.38	9.81	9.98	10.25
300	572	10.73	10.2	10.34	10.54
400	752	10.93	10.53	10.6	10.79
500	932	11.16	10.87	10.89	11.06
600	1112	11.35	11.06	11.09	11.3
700	1292	11.68	11.33	11.45	11.61
800	1472	12.18	11.76	11.93	12.06
900	1652	12.58	12.24	12.53	12.58
998	1810	13.02	--	--	--
1000	1832	--	12.74	13.05	13.12

The E-BRITE® alloy's low carbon limit and limitations on nickel and copper (individually and combined) are relaxed in the alloy of the present invention as broadly described herein. It is believed that such variation would have no appreciable influence on the thermal expansion properties of the alloy.

5   It also is believed that including at least one of niobium, titanium, and tantalum in the alloy of the present invention so as to satisfy the equation

$$0.4 \leq (\%Nb + \%Ti + \tfrac{1}{2}(\%Ta)) \leq 1$$

would not effect the CTE of the alloy substantially. All CTE values in Table 18 are within about 25% of 11 x 10^{-6} per °C, which is the approximate CTE of YSZ

10   between 20°C (68°F) and 1000°C (1832°F).

Accordingly, the above testing results demonstrate that the ferritic stainless steel of the present has improved high temperature mechanical properties relative to a standard ferritic stainless steel. For example, relative to

5   E-BRITE® ferritic stainless steel, the stainless steel of the present invention exhibits improved microstructural stability, enhanced mechanical properties, and greater resistance to creep at high temperatures.

Any suitable conventional melting and refining practices may be used to prepare slabs or ingots of the steel of the present invention. The slabs or

10   ingot may be further processed in a conventional manner to product such as strip, sheet, or plate, solution annealed and, optionally, precipitation heat treated. For the contemplated fuel cell application, the steel may be precipitation heat treated at the use temperature (about 1600 to 1830°F (871 to 999°C)). When lower use temperatures are involved, it may be desirable to precipitation harden

15   the steel by exposing it to a temperature of about 1600°F (871°C) for a time sufficient to suitably strengthen the material.

The steel may be fabricated into components for SOFC's including a stabilized zirconia-containing electrolyte. Such components include separators and interconnects for SOFC's including electrolyte containing stabilized zirconia.

20   The steel also may be processed into components for oxygen sensor devices including stabilized zirconia, or into articles for other high temperature applications, such as for use in high temperature furnace hardware and

equipment for handling molten copper and other molten metals. As an example, SOFC's including the ferritic stainless steel of the present invention may include a ceramic anode, a ceramic cathode, and a stabilized zirconia electrolyte intermediate the anode and cathode. The SOFC's also may include at least one

5   of an interconnect and a separator including the present ferritic stainless and disposed adjacent the ceramic electrolyte.

It is to be understood that the foregoing description illustrates those aspects of the invention relevant to a clear understanding of the invention. Certain aspects of the invention that would be apparent to those of ordinary skill

10   in the art and that, therefore, would not facilitate a better understanding of the invention have not been presented in order to simplify the present description. Although the present invention has been described in connection with certain embodiments, those of ordinary skill in the art will, upon considering the foregoing description, recognize that many modifications and variations of the

15   invention may be employed. It is intended that all such variations and modifications of the inventions be covered by the foregoing description and following claims.